

**RESERVE COPY.**

**PATENT SPECIFICATION**

**1,026,105**



**NO DRAWINGS**

**1,026,105**

*Date of Application and filing Complete Specification: Nov. 8, 1963.*

**No. 44133/63.**

*Four Applications made in United States of America (Nos. 236,404, 236,410,  
236,411 and 236,413) on Nov. 8, 1962.*

*Complete Specification Published: April 14, 1966.*

*© Crown Copyright 1966.*

**Index at acceptance:—C2 C(1Q1A, 1Q6A1, 1Q6A2, 1Q8A, 1Q11B); B1 E3B1; C1 A(D16,  
G4) AG4D16**

**Int. Cl.:—C 07 c // B 01 j, C 01 f**

**COMPLETE SPECIFICATION**

**Process for preparing Vinyl Fluoride and 1,1-Difluoroethane**

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is directed to a process for reacting acetylene with hydrogen fluoride in the vapour phase and in the presence of aluminium fluoride as catalyst to form vinyl fluoride and 1,1-difluoroethane.

Aluminium fluoride has, of course, been known for many years. Unlike many other compounds however, the aluminium fluoride known to the art has only one crystalline form named the alpha form by analogy with the high-temperature stable form of alumina and this form is a relatively poor catalyst for the reaction of hydrogen fluoride with acetylene for a number of reasons.

There are several catalysts known for the vapour phase reaction of acetylene with hydrogen fluoride besides the known aluminium fluoride; for example, aluminium oxide, aluminium sulphate and the like. All the known solid catalysts have the disadvantage of either giving poor conversions at reasonable feed rates or undesirably high yields of tars and other by-products.

A process for reacting acetylene with hydrogen fluoride over aluminium oxide or aluminium fluoride as catalyst is described in U.S. Patent Specification No. 2,471,525. While the aluminium oxide catalyst described in this Specification is a usable catalyst system, it has the disadvantage, in the initial stages of the process, of giving rise to water and considerable amounts of tars and gaseous by-products. Tars lead to much pluggage of equipment, causing considerable lost time.

Water is undesirable since it combines with

unreacted hydrogen fluoride to form a highly corrosive liquid which causes severe damage to manufacturing equipment. Also, the yields of vinyl fluoride and 1,1-difluoroethane are relatively low over a fresh aluminium oxide catalyst system although the conversion of acetylene to other, undesired gaseous hydrocarbon by-products is reasonably high. These gaseous hydrocarbons not only waste acetylene but also cause considerable difficulty in the separation and purification of the desired products from the reaction mixture.

The present invention is directed to a process for preparing vinyl fluoride and 1,1-difluoroethane which comprises passing a mixture of hydrogen fluoride and acetylene at a temperature of from 250°C to 400°C and at a pressure of from 0.1 to 4 atmospheres absolute over beta or gamma-aluminium fluoride catalyst or a mixture thereof with delta-aluminium fluoride catalyst, the mixture of hydrogen fluoride and acetylene having a molar ratio of from 1 to 5 moles of hydrogen fluoride per mole of acetylene and the feed rate of acetylene in the mixture being from 10 to 4000 millilitres, measured at standard conditions, per gram of catalyst per hour, and recovering vinyl fluoride and 1,1-difluoroethane from the reaction mixture.

The preparation of the beta aluminium fluoride and its characteristics are described in our co-pending Patent Application No. 48869/64 (Serial 1026106).

Gamma-aluminium fluoride, so-called by analogy with the corresponding form of alumina can be prepared by heating  $\beta$ -aluminium fluoride trihydrate at a temperature of from 150°C to 450°C until water ceases to be evolved therefrom.

Gamma-aluminium fluoride has the  $VF_3$  structure. There are holes in the crystal structure formed by eight  $AlF_3$  molecules but these are too small to occlude water or hydrogen fluoride. There may be a maximum of

50

55

60

65

70

75

80

85

90

about 0.25 mole of water per molecule of aluminium fluoride in the crystal.

The only method presently known to us for preparing pure gamma-aluminium fluoride consists in dehydrating beta-aluminium trifluoride trihydrate at 150°C to 450°C. At least 150°C is preferred to decompose the trihydrate. Dehydration temperatures greater than about 450°C can be used but increasing amounts of undesired  $\alpha$ -aluminium fluoride are formed. At temperatures above 600°C the high temperature  $\alpha$ -aluminium fluoride is the predominant product.

Beta-aluminium trifluoride trihydrate is prepared by the method described by Ehret and Frere in J. Amer. Chem. Soc., 67, 64 (1945). More specifically, it is prepared by dissolving aluminium or aluminium oxide in aqueous hydrofluoric acid and heating the solution at 60—100°C for about 24 hours which causes the di-trihydrate to precipitate. If the disso-

lution and precipitation are carried out at 10—15°C an aluminium fluoride hydrate  $\text{AlF}_3 \cdot 9\text{H}_2\text{O}$  precipitates which loses six moles of water on standing in air to form  $\alpha$ -aluminium trifluoride trihydrate; the alpha and beta-aluminium trifluoride trihydrates are readily distinguished by their X-ray diffraction patterns. The pattern for beta-aluminium trifluoride trihydrate is given on ASTM Card 9—108.

Gamma-aluminium fluoride belongs to space group  $D_{3d}^6 - R\bar{3}c$ , has unit cell parameters  $a = 5.0$  Å and  $c = 12.28$  Å and a unit cell volume of 3459 Å<sup>3</sup>, contains six molecules per unit cell and has a calculated density of 3.130 g./cc.

The X-ray diffraction line positions and intensities of gamma-aluminium fluoride are given below in Table I.

TABLE I  
Spacings and Intensities of gamma-AlF<sub>3</sub>

d(Å)	Intensity	(hkl)
3.537	vst	(200)
2.501	w	(220)
2.134	vw	(311)
2.042	w	(222)
1.768	st	(400)
1.623	w	(331)
1.583	mst	(420)
1.444	w	(422)
1.363	vw	(511) (333)
1.250	vw	(440)
1.197	w	(531)
1.179	vw	(600) (422)
1.118	vw	(620)
1.066	vw	(622)
1.021	vw	(444)
0.981	w	(640)
0.946	w	(642)
0.884	w	(800)
0.858	vw	(820) (644)
0.834	vw	(822) (660)

st = strong, m = medium, w = weak, v = very.

- 5 The mixture of beta,gamma and delta-aluminium fluoride catalysts can be obtained by heating aluminium chloride with anhydrous hydrogen fluoride at from 25°C to 380°C until replacement of chlorine by fluorine is substantially complete.
- 10 The preparation of an aluminium fluoride catalyst by treatment of aluminium chloride with hydrogen fluoride is described in U.S. Patent Specification No. 2,673,139. As prepared, the catalyst described in U.S. 2,673,139 is amorphous to X-rays. Furthermore, the disclosure of U.S. 2,673,139 gives no reason to believe that the aluminium fluoride catalyst 15 as prepared is different from ordinary aluminium fluoride except that the crystal size is too small to give X-ray diffraction patterns. It has now been found however that, if the catalyst described in U.S. 2,673,139 is held 20 at an elevated temperature, say 350—400°C., for sufficient time, crystals of sufficient size form to give X-ray diffraction patterns. The

crystals thus detected are found to differ from the known form of aluminium fluoride and indeed, the crystals of the catalyst prepared in U.S. 2,673,139 are found to be a mixture of three previously undescribed crystalline forms of aluminium fluoride, each form being entirely different from the other two forms as well as from the known alpha form of aluminium fluoride. Two of these forms are the aforementioned beta and gamma-forms. The third form, delta-aluminium fluoride (also an undescribed form) belongs to space group O<sub>h</sub> —Imcm, has the unit cell parameter a = 14.34 Å, has a unit cell volume of 29,500 Å<sup>3</sup>, contains 64 molecules of AlF<sub>3</sub> per unit cell and has a calculated density of 3.025 g./cc. The X-ray diffraction line positions and intensities of delta-aluminium fluoride are given below in Table II.

TABLE II  
Spacing and Intensities of delta-AlF<sub>3</sub>

d(Å)	Intensity	(hkl)
5.856	m	(211)
5.071	m	(220)
4.139	vst	(222)
3.833	st	(321)
3.585	mw	(400)
3.380	w	(411) (330)
3.207	vst	(420)
3.057	m	(332)
2.927	w	(422)
2.618	vw	(521)
2.459	vw	(530) (433)
2.390	vw	(600) (442)
2.267	vw	(620)
2.213	vw	(541)
2.162	vw	(622)
2.070	vw	(444)
2.028	m	(710) (550) (543)
1.951	mw	(721) (633) (552)
1.916	m	(642)
1.821	vw	(732) (651)
1.792	w	(800)
1.765	w	(811) (741) (554)
1.739	m	(280) (644)
1.714	vw	(653)
1.690	m	(822) (660)
1.667	w	(831) (750) (743)
1.645	m	(662)
1.624	vw	(752)
1.603	m	(840)

st=strong, m=medium, w=weak, v=very.

The catalytic mixture of beta-, gamma- and delta-aluminium fluorides can be also prepared from aluminium oxide by passing anhydrous hydrogen fluoride over an aluminium oxide catalyst at from 200° to 500°C. until from 0.3 moles to 6 moles of hydrogen fluoride per mole of aluminium oxide have reacted with the aluminium oxide. In this step there appears to be a reaction between the aluminium oxide and the hydrogen fluoride because water is formed in the course of the action. X-ray diffraction studies of the treated catalyst indicate that aluminium fluoride is formed. When sufficient hydrogen fluoride is added, the aluminium oxide ceases to react further. Although it is preferred to completely react the aluminium oxide with hydrogen fluoride, corresponding benefit is gained by partial reaction of the aluminium oxide catalyst with hydrogen fluoride. Partial reaction of aluminium oxide with hydrogen fluoride during the pretreatment results in less water, by-products and tar formation during the subsequent reaction of acetylene with hydrogen fluoride. To completely react aluminium oxide with hydrogen fluoride requires six moles of hydrogen fluoride per mole of aluminium oxide. Since the reaction of gaseous flowing hydrogen fluoride with aluminium oxide is usually incomplete, the best results are obtained if about 6.5 moles of hydrogen fluoride per mole of aluminium oxide are used. Naturally, more than 6.5 moles of hydrogen fluoride may be used and as high as 18 moles of hydrogen fluoride per mole of aluminium oxide have been used, but the excess hydrogen fluoride passes through largely un-reacted and gives little additional useful advantage. However, there is no useful benefit to the catalyst system if less than 0.3 moles of hydrogen fluoride per mole of aluminium oxide react.

The pretreatment of the aluminium oxide catalyst is carried out at from 200° to 500°C. Below 200°C. essentially no water evolution occurs. Any water which may be formed is apparently retained in the solid material. This leads to structural instability of the catalyst particles. The catalyst thus becomes difficult to remove from the reactor. At temperatures above 500°C. a less active form of the catalyst is obtained, apparently due to changes in crystal form or the like which affects its catalytic activity. It is preferred to carry out the catalyst pretreatment at 300°C. The rate of addition of hydrogen fluoride to aluminium oxide is not an important factor if the flow is sufficiently slow for a majority of the hydrogen fluoride to react. Feed rates of from 0.01 parts to 2.0 parts of hydrogen fluoride per part of aluminium oxide per hour have been used and from 0.09 to 0.26 part of hydrogen fluoride per part of aluminium oxide per hour are most satisfactory. Under these conditions, water ceases to be formed after about 6.5

moles of hydrogen fluoride have been added, indicating that six moles have reacted. As a general procedure, the best catalyst is obtained if hydrogen fluoride is added until water ceases to be formed.

70

The pretreatment of the aluminium oxide is preferably, although not essentially, carried out in a flow system. The advantage of the flow system is that the water which is formed can be driven out of the reaction system by the flow of the hydrogen fluoride gas. During the pretreatment, it is preferable as a matter of convenience to neutralize the water-hydrogen fluoride off gases. The treated solid may be swept with an inert gas such as nitrogen to remove any remaining water and excess hydrogen fluoride if desired, although it is not essential to do so.

75

The form of aluminium oxide used has some importance. The so-called "activated aluminas" are the more preferred catalysts. Fused alumina and like forms are of little use because they do not form useful catalysts for the reaction of acetylene with hydrogen fluoride.

80

In the disclosure of U.S. 2,471,525, it was reasoned that if any reaction at all occurred between the aluminium oxide and hydrogen fluoride, that an aluminium oxyfluoride was formed on the surface of the catalyst. The disclosure also stated that the quantity of aluminium fluoride formed was exceedingly small. It has been found that the present pretreatment of aluminium oxide with hydrogen fluoride does lead to formation of aluminium fluoride. If sufficient hydrogen fluoride is used, as in the preferred mode of pretreatment, the aluminium oxide appears to be essentially completely converted to aluminium fluoride. X-ray diffraction patterns of the resulting catalyst material indicate that a mixture of all four crystalline forms  $\alpha$ ,  $\beta$ , gamma and delta of aluminium fluoride are present which as described before are readily distinguished by their X-ray diffraction patterns.

90

The catalyst obtained by the present pretreatment is a surprisingly effective catalyst for the reaction of acetylene with hydrogen fluoride. Since, beta, gamma, and delta-forms of aluminium fluoride are converted to  $\alpha$ -aluminium fluoride by heating above 600°C., the loss of catalyst activity due to overheating may be due to this conversion.

95

In the process of the present invention beta-, gamma- or delta-aluminium fluoride or the mixtures thereof in any suitable form such as powder, pellets or the like is placed in a reactor fitted with means for contacting gases with solids. The reactor and catalyst are heated to the desired reaction temperature and a mixture of anhydrous hydrogen fluoride and acetylene is passed over the catalyst. The reaction mixture of hydrogen fluoride and acetylene may be preheated. However, pre-

100

105

110

115

120

125

130

- heating the reaction mixture, although preferred, is not necessary to effect the desired reaction. The product issuing from the reactor consists of a mixture of hydrogen fluoride, acetylene, vinyl fluoride and 1,1-difluoroethane and, on some occasions, a number of other trace by-products. This mixture is separated into its constituent parts by any convenient means. Distillation is one such means; hydrogen fluoride (b.p. 19.4°C.) is easily separated from acetylene (b.p. -84°C.), vinyl fluoride (b.p. -72.2°C.) and 1,1-difluoroethane (b.p. -24.7°C.) and the organic materials are separable by properly designed distillation equipment under pressure. Alternate methods, known to the art, exist for separating the reaction products. The hydrogen fluoride and acetylene recovered may be recycled if desired.
- The reaction is carried out at from about 250°C. to about 400°C. At temperatures below about 250°C. the reaction is too slow to be useful commercially. At temperatures above about 400°C., by-product formation becomes increasingly rapid. Above 500°C. the catalyst is slowly converted to the less active  $\alpha$ -form and this is to be avoided. Although the active inventive forms can be converted to the less active  $\alpha$ -form by heating, there is no way known for converting the less active  $\alpha$ -form back to the more active forms. Thus, once the catalyst is overheated and loses its activity, the activity cannot be regained.
- The mole ratio of hydrogen fluoride to acetylene may vary from about one to about five. When the ratio is much below one the conversion of acetylene is undesirably low, resulting in excessively large amounts of acetylene which must be removed or recovered and recycled. Of course, some vinyl fluoride and 1,1-difluoroethane are formed but the process is commercially unattractive. The increasing amounts of hydrogen fluoride resulting from mole ratios much above five have little practical effect on conversion of acetylene to products. The larger amounts of hydrogen fluoride also result in larger recovery and recycle streams with no practical advantage.
- Since hydrogen fluoride is not monomeric in the vapor phase below about 60°C., the mole ratio cannot be determined from volume ratios unless the molecular weight of hydrogen fluoride vapor is taken into account. The mole ratio is best calculated from the weight of hydrogen fluoride fed per unit time. It is naturally understood that the mole ratio is for moles of monomolecular hydrogen fluoride per mole of acetylene.
- Reaction pressures of from 0.1 to 4 atmospheres may be used. Generally it is preferred to operate at one atmosphere or above due to the increased difficulties of operating at subatmospheric pressure.
- The feed rates of acetylene, using the mole ratios of reactants as discussed above, may be varied from about 10 to about 4000 milliliters of acetylene per gram of catalyst per hour. The volume of acetylene indicated is determined at 25°C. and one atmosphere pressure regardless of the reaction temperature and pressure used. The weight of the catalyst is based on the inventive aluminum fluoride used excluding the weight of binders and the like which may be used to prepare pellets or similar forms. Contact times or residence times vary with feed rate, temperature and pressure. Since it is well known that determination of gas temperature in flow systems is subject to many errors and the calculation of contact times to many others, it is preferred to define the present process on the basis of the readily determined feed rates defined above which are not subject to these undetermined errors.
- It has been found that increasing the reaction pressure above one atmosphere, keeping feed rate, mole ratios and temperatures constant, increased the conversion of acetylene to products. The relative yield of 1,1-difluoroethane compared to vinyl fluoride is not materially affected by a pressure increase. Hence, there is an economic advantage gained in higher conversions and productivity and smaller recycle streams by operating at superatmospheric pressures.
- The preferred conditions of the present process are 300-350°C., 1.3 moles of hydrogen fluoride per mole of acetylene and 2-4 atmospheres absolute. Acetylene feed rates of less than 400 ml./grams catalyst/hour are preferred. These preferred conditions lead to optimum yields of vinyl fluoride.
- The reactor and other equipment must be resistant to the action of hydrogen fluoride. If dry, steel may be used although it is preferred to use stainless steel, nickel or the high nickel alloys such as "Inconel" (trade mark) or "Monel" (trade mark) metals. The reactor may be heated in any manner known to the art which allows sufficient temperature control such as electric heaters, molten salt baths and the like. The starting materials should be reasonably anhydrous. Commercial anhydrous hydrogen fluoride contains slight traces of water which may be tolerated. Acetylene often contains acetone and other impurities, especially when it is stored in cylinders in acetone solution. Methods for removing acetone and other impurities and for drying acetylene are well known to the art. (See U.S. 2,716,142, col. 3, line 72 to col. 4, line 5). The acetylene used in the examples which follow was thus purified.
- If using a pretreated aluminum oxide catalyst the inventive process has the following advantage over the prior art.
- While the disclosure in the U.S. 2,471,525 indicated that there might be some slight reaction between hydrogen fluoride and alu-

5 minum oxide catalyst, the disclosure gave no indication that their aluminum oxide catalyst has an induction period during which yields of vinyl fluoride and 1,1-difluoroethane are low, during which tar and gaseous by-product formation is undesirably high and during which water formation takes place. While water formation is readily explained by reaction between hydrogen fluoride and aluminum oxide, the low initial yields of vinyl fluoride and 1,1-difluoroethane and high yields of tar and gaseous by-products are not readily explained unless it is assumed that aluminum oxide is a poor catalyst for the reaction of 10 hydrogen fluoride with acetylene and a good catalyst for converting acetylene to gaseous by-products and higher molecular weight polymeric products. As is shown in the examples which follow, pretreated aluminum oxide catalyst does away with this induction period and the problems it introduces. The gaseous by-products consist of alkanes and alkenes such as ethane, ethylene, propane, propylene, butylene and the like.

15 25 Vinyl fluoride is useful for preparing polymers, especially polyvinyl fluoride, a commercial product. 1,1-Difluoroethane is useful as a refrigerant, propellant and as an intermediate for preparing chlorodifluoroethane (U.S. 2,899,472), vinylidene fluoride (U.S. 2,551,573) and other valuable products (U.S. 2,417,059; 2,549,767; 2,469,290). 1,1 - Difluoroethane may also be converted to vinyl fluoride by any of several known processes if desired (U.S. 2,599,631; 2,674,632).

20 In order that the invention may be more fully understood the following Examples are given by way of illustration only.

25 EXAMPLE I

30 35 40 In a large polyethylene beaker, 800 g. of

48% hydrofluoric acid was diluted with water to a volume of 3200 ml. Hydrated alumina (400 g., "Alcoa" (trade mark) C-33 grade from the Aluminium Company of America) was added slowly to the acid at a rate which increased the temperature of the reaction mass to 60°C. After all of the alumina was added, heat was applied for 24 hrs. to maintain the temperature at 60°C during which time precipitation occurred. About one-half of the original volume remained. The slurry was filtered while hot and the beta-aluminium trifluoride trihydrate collected was washed with water, then dried at 100°C for four hours. The dry beta-aluminium trifluoride trihydrate was identified by its X-ray diffraction pattern. It was converted to gamma-aluminium fluoride by heating in a muffle furnace at 400°C for four hours.

50 55 60 65 70 75 80

## EXAMPLE II

A vertically mounted, tubular stainless steel reactor of one inch (inside diameter) was fitted for admitting gaseous acetylene and hydrogen fluoride at the bottom and allowing products to be removed at the top. Gamma-aluminum fluoride powder (110.9 g. unless otherwise noted) was placed in the reactor forming in a bed 16 inches deep. The reactor was heated in a molten salt bath and a mixture of anhydrous hydrogen fluoride and acetylene was passed into the reactor at atmospheric pressure under the several conditions shown below. The effluent product was scrubbed with water and aqueous alkali to remove hydrogen fluoride, then analyzed for convenience by means of a mass spectrometer with the results shown below. The hydrogen fluoride, vinyl fluoride and 1,1-difluoroethane may also be separated by distillation if desired.

## Conditions

Example	Mole Ratio HF/C <sub>2</sub> H <sub>2</sub>	Temperature °C.	Acetylene Feed Rate ml./g. catalyst/hr.	Remarks
IIa	1.15	315	108.4	—
b	2.28	315	71.6	—
c	2.24	315	97.2	—
d	2.24	255	148.7	82 g. catalyst powder
e	1.3	315	232.0	68 g. catalyst pellets
f	1.3	350	153.8	88 g. catalyst powder
g	1.4	370	135.4	85 g. catalyst powder

## RESULTS

Example	IIa	b	c	d	e	f	g
<i>Mole % Products</i>							
<i>Vinyl Fluoride</i>	71.4	58.2	56.6	9	84	76	78
<i>1,1-Difluoroethane</i>	9.2	35.7	39.4	67	9	16	14
<i>Acetylene</i>	18.4	4.1	2.0	24	8	7	8
<i>Ethylene</i>	1.0	2.0	2.0	trace	trace	trace	trace
<i>% Conversion of Acetylene</i>	81.6	95.9	98.0	76	92	92	92
<i>% Yield (based on acetylene converted)</i>							
<i>Vinyl Fluoride</i>	87.5	60.6	57.8	11.8	91.3	81.7	84.8
<i>1,1-Difluoroethane</i>	11.5	37.2	40.4	88.2	8.7	18.3	15.2

## EXAMPLE III

In order to illustrate the superiority of gamma-aluminum fluoride as a catalyst over the previously known  $\alpha$ -aluminum fluoride, the following examples were carried out in the apparatus described in the previous examples.  $\alpha$ -Aluminum fluoride (209.7 g.), used as granulated material prepared by

crushing pellets obtained from Harshaw Chemical Co., was placed in the reactor. The reactor was then heated in the molten salt bath as before and mixtures of anhydrous hydrogen fluoride and acetylene were passed into the reactor at atmospheric pressure. The reaction conditions used and the results obtained are given below.

Example	Mole Ratio HF/C <sub>2</sub> H <sub>2</sub>	CONDITIONS	
		Temperature °C.	Acetylene Feed Rate ml./g. catalyst/hr.
IIIa	2.4	315	26.1
b	2.4	315	30.0
c	2.4	315	43.8
d	1.3	320	43.5
e	1.3	346	38.8

Example	RESULTS				
	IIIa	b	c	d	e
<i>Mole % Products</i>	28.0	39.8	34.1	42.0	52.0
1,1-Difluoroethane	21.4	22.1	17.5	13.8	10.7
Acetylene	49.9	36.8	47.6	40.5	34.8
Propane	0.01	0.10	0.01	0.01	0.01
Ethylene	0.8	0.6	0.4	1.7	3.8
Ethane	0.01	0.1	0.06	0.03	0.08
% Conversion	50.1	63.2	52.4	59.5	65.2
% Yield (based on acetylene converted)					
Vinyl Fluoride	55.4	63.0	65.0	70.6	79.8
1,1-Difluoroethane	42.7	35.0	33.5	23.2	16.4

The reaction conditions in Example III a—e were selected to obtain optimum results using the alpha-aluminum fluoride catalyst.

5 Slower feed rates were used in Example III a—e using the alpha-aluminum fluoride catalyst than in Examples II a—g (using the gamma-aluminum fluoride catalyst) in order to obtain reasonable conversion. Higher conversions could be obtained than those in Examples II a—g (using even slower feed rates) but the yields would suffer. It should also be noted that lower feed rates increase somewhat the opportunity for by-product formation.

10 Comparing Examples III a—e with Examples II a—g shows that the commercial  $\alpha$ -form of aluminum fluoride is a much poorer catalyst than the new gamma-form of aluminum fluoride. The known alpha-aluminum

15 fluoride causes conversions of acetylene approximately 50% lower at feed rates which are at least three to five times slower, i.e., production rates are from 1/6 to 1/10 that of the new catalyst. Since both the  $\alpha$ - and the gamma-forms of aluminum fluoride are prepared from  $\beta$ -aluminum fluoride trihydrate, the only difference being the temperature to which the trihydrate is heated, it can be stated that the new gamma-form is inherently at least six to ten times more active than the known  $\alpha$ -form. This is an entirely unexpected and surprising result.

#### EXAMPLE IV

20 Using the equipment and catalyst of Examples II a—g, a reaction was carried out at 330°C., using an HF/acetylene mole ratio of 1.28/1, a feed rate of 250 ml. reactants (at 25°C. and one atmosphere)/gram catalyst/hr. and a reaction pressure of 2.7 atm. abs. The results are shown below.

25

30

35

40

## RESULTS

## Mole % Products

<i>Vinyl Fluoride</i>	77.9
<i>1,1-Difluoroethane</i>	11.6
<i>Acetylene</i>	6.0
<i>Ethylene</i>	3.7
<i>Propylene</i>	0.1
<i>Others</i>	0.2
<i>% Conversion</i>	94.2

## % Yield

<i>Vinyl Fluoride</i>	79.8
<i>1,1-Difluoroethane</i>	11.9
<i>By-products</i>	4.1

## EXAMPLE V

5 Powdered gamma - aluminum fluoride (5.0 grams) was placed in a  $0.9 \times 20.3$  cm. tubular reactor fitted in the same manner as the previous examples. Acetylene and hydrogen fluoride were passed into the reactor which was heated at  $325^{\circ}\text{C}$ . The mole ratio was 1.3 moles HF per mole of acetylene and the feed rate of acetylene was 3600 ml. (at standard conditions)/gram catalyst/hr. The reaction pressure was 3 atm. abs. The product was recovered as before. The results are shown below.

10

## RESULTS

## Mole % Product

<i>Vinyl Fluoride</i>	79.5
<i>1,1-Difluoroethane</i>	16.7
<i>Acetylene</i>	3.0
<i>Ethylene</i>	0.9
<i>% Conversion</i>	97.0
<i>% Yield</i>	
<i>Vinyl Fluoride</i>	81.2
<i>1,1-Difluoroethane</i>	17.0
<i>Ethylene</i>	1.8

**EXAMPLE VI***Preparation of Catalyst*

This example follows in essential detail the procedure described in U.S. 2,673,139.

- 5      Powdered aluminum chloride (200 g.) was placed in a one inch (inside diameter) stainless steel tubular reactor and anhydrous hydrogen fluoride diluted with nitrogen was fed vapor phase into the reactor until 140 g.  
 10     of hydrogen fluoride had been added while the temperature was maintained below 80°C. The hydrogen fluoride-nitrogen feed was maintained while the reactor was heated slowly to 380°C. The system was then cooled in a hydrogen fluoride-nitrogen atmosphere. X-ray diffraction showed this catalyst to be  
 15     amorphous.

**EXAMPLE VII**

A vertically mounted, tubular "Inconel" reactor of one inch (inside diameter) was fitted at the bottom to allow controlled flows of gaseous acetylene and anhydrous hydrogen fluoride to enter and, at the top, to allow products to be removed. The catalyst prepared in Example VI (132 g.) was placed in the reactor. The reactor was then placed in a molten salt bath at the desired reaction temperature. Hydrogen fluoride and acetylene were mixed in the desired proportions and passed into the reactor at approximately atmospheric pressure under the conditions shown below. The results are also shown below.

20  
25  
30

**CONDITIONS**

Example	Mole Ratio HF/C <sub>2</sub> H <sub>2</sub>	Temp. °C.	Acetylene Feed Rate ml.*/g. catalyst /hr.
VIIa	1.3	350	47.8
b	1.3	350	71.4
c	2.5	350	31.4
d	4.2	350	62.9
e	1.3	400	47.8
f	1.3	400	71.4
g	2.24	250	36.4
h	1.3	315	54.4
i	1.3	315	114.7
j	2.24	315	35.8

\*. at 25°C. and one atmosphere.

## RESULTS

Example	VIIa	b	c	d	e	f	g	h	i	j
<i>Mole % Product</i>										
<i>Vinyl Fluoride</i>	68.6	63.8	72.4	67.6	66.7	65.8	25.3	77.8	68.8	70.0
<i>1,1-Difluoroethane</i>	19.1	26.3	18.0	26.3	18.7	9.5	63.4	11.6	2.7	3.5
<i>Acetylene</i>	4.5	3.0	4.8	2.8	5.7	12.5	11.3	10.7	28.5	24.3
<i>Propylene</i>	0.5	0.3	0.08	0.1	0.01	0.07	—	—	—	0.4
<i>Propane</i>	0.3	0.1	0.03	—	0.07	0.07	—	—	—	—
<i>Ethylene</i>	6.9	6.1	3.8	3.1	8.7	10.5	—	—	—	1.7
<i>Ethane</i>	0.3	0.3	0.04	0.09	0.2	0.4	—	—	—	0.08
<i>% Conversion</i>	95.5	97.0	96.2	97.2	94.3	87.5	88.7	89.3	71.5	76.1
<i>% Yield</i>										
<i>Vinyl Fluoride</i>	71.5	65.8	76.1	69.5	70.7	75.2	28.5	87.1	95.2	90.6
<i>1,1-Difluoroethane</i>	20.0	27.1	18.9	27.1	19.8	10.8	71.5	13.0	3.8	4.5

## EXAMPLE VIII

Using the equipment and catalyst of Example VII, a reaction was carried out at 335°C., using an HF/acetylene mole ratio of

1.3/1, a feed rate of 398 ml. reactants (at 25° C. and one atmosphere)/g. catalyst/hr. and a reaction pressure of 2.7 atm.abs. The results are shown below.

## RESULTS

*Mole % Products*

<i>Vinyl Fluoride</i>	80.1
<i>1,1-Difluoroethane</i>	8.0
<i>Acetylene</i>	9.2
<i>Ethylene</i>	2.0
<i>Propylene</i>	0.1
<i>Ethane</i>	0.06
<i>Others</i>	0.58
<i>% Conversion</i>	90.9
<i>% Yield</i>	
<i>Vinyl Fluoride</i>	86.3
<i>1,1-Difluoroethane</i>	8.6
<i>By-Products</i>	2.5

## EXAMPLE IX

5 The catalyst prepared in Example VI (6.0 g.) was placed in an  $0.9 \times 20.3$  cm. tubular reactor fitted in the same manner as the previous examples. Acetylene and hydrogen fluoride were passed into the reactor which was heated at  $325^{\circ}\text{C}$ . The mole ratio was 1.3 moles HF per mole of acetylene and the feed rate of acetylene was 1895 ml. (at standard conditions)/gram catalyst/hr. The reaction pressure was 30 psig. The product was recovered as before. The results are shown below. 10

## RESULTS

*Mole % Product*

<i>Vinyl Fluoride</i>	74.0
<i>1,1-Difluoroethane</i>	19.0
<i>Acetylene</i>	7.0
<i>% Conversion</i>	93.0
<i>% Yield</i>	
<i>Vinyl Fluoride</i>	79.6
<i>1,1-Difluoroethane</i>	20.4

15

## EXAMPLE X

A vertically mounted, tubular stainless steel reactor of one inch (inside diameter) was fitted for admitting gaseous acetylene and hydrogen fluoride at the bottom and allowing products to be removed from the top. Beta-Aluminum fluoride (61 g.) was placed in the

reactor to form a bed 14 inches deep. The reactor was immersed in a molten salt bath, swept with nitrogen, and mixtures of acetylene and hydrogen fluoride were fed into the system at atmospheric pressure under the conditions shown below. The results are also shown below. 25

Example	CONDITIONS		
	Mole Ratio HF/C <sub>2</sub> H <sub>2</sub>	Temperature °C.	Acetylene Feed Rate ml./g. catalyst/hr.
Xa	2.4	315	148.8
b	2.4	315	89.7
c	2.24	350	172.5
d	1.3	350	163.4

## RESULTS

Example	Xa	b	c	d
<i>Mole % Products</i>				
Vinyl Fluoride	81.0	72.3	64	81
1,1-Difluoroethane	5.5	18.0	35	17
Acetylene	10.3	7.9	1.3	2
Propylene	0.3	0.1	—	—
Ethane	0.1	0.01	—	—
Ethylene	2.9	1.6	—	—
% Conversion	90.0	92.2	98.1	98.0
<i>% Yield (based on acetylene converted)</i>				
Vinyl Fluoride	86.6	76.9	64.8	82.7
1,1-Difluoroethane	5.9	19.2	35.2	17.3

EXAMPLE XI  
Using the equipment and catalyst of 1.3/1, a feed rate of 398 ml. reactants (at 25°C. and one atmosphere)/gram catalyst/hr. Examples X a reaction was carried out at and a reaction pressure of 2.7 atm. abs. The 5 330°C., using a HF/acetylene mole ratio of results are shown below.

## RESULTS

<i>Mole % Products</i>	
Vinyl Fluoride	80.1
1,1-Difluoroethane	8.0
Acetylene	13.6
Ethylene	2.6
Butylene	0.04
Propylene	0.2
Ethane	0.1
Others	0.3
% Conversion	87.4
<i>% Yield</i>	
Vinyl Fluoride	84.7
1,1-Difluoroethane	8.5
By-products	3.1

**EXAMPLE XII**

Powdered beta-aluminum fluoride (6.0 g.) was placed in a  $0.9 \times 20.3$  cm tubular reactor fitted in the same manner as the previous examples. Acetylene and hydrogen fluoride were passed into the reactor which was heated

at  $325^{\circ}\text{C}$ . The mole ratio of HF to acetylene was 1.3 and the feed rate of acetylene was 3000 ml. (at standard conditions)/gram catalyst/hr. The reaction pressure was 3 atm. abs. The product was recovered as before. The results are shown below.

10

**RESULTS***Mole % Product*

<i>Vinyl Fluoride</i>	74.0
<i>1,1-Difluoroethane</i>	25.0
<i>Acetylene</i>	1.0
<i>% Conversion</i>	99.0
<i>% Yield</i>	
<i>Vinyl Fluoride</i>	74.5
<i>1,1-Difluoroethane</i>	25.5

**EXAMPLE XIII****15 Catalyst Pretreatment**

A. Activated alumina (60 g., grade F-10, Alcoa) was placed in a one inch (inside diameter) stainless steel pipe reactor fitted with means for admitting hydrogen fluoride and nitrogen and removing off-gases. The reactor

20 was immersed in a molten salt bath at  $300^{\circ}\text{C}$ . and anhydrous hydrogen fluoride was fed over the alumina (229 g., 7.30 moles per mole of alumina) in a period of five and one-half hours. Nitrogen was then passed through the reactor to remove excess hydrogen fluoride and other volatile materials. After cooling, the treated alumina was found to be identical in appearance to the original alumina. Both

30 color and geometry were retained.

B. Example XIII—A was repeated at  $175^{\circ}\text{C}$ . After cooling it was found that the treated alumina had both aggregated and pulverized. It was difficult to remove from the reactor.

C. Example XIII—A was repeated by treating 236 g. of alumina with 510 g. of hydrogen fluoride (11.0 moles per mole of alumina) at  $300^{\circ}\text{C}$ . over a 23 hr. period. The product weighed 337.8 g. It retained its color and form.

D. Example XIII—C was repeated using 302 g. of hydrogen fluoride (6.5 moles per mole of alumina). The product weighed 337.6. It retained its color and form.

Comparison of Examples XIII—C and XIII—D shows that excess hydrogen fluoride over 6.5 moles per mole of alumina has no apparent effect on the product.

45

**EXAMPLE XIV**

The catalyst prepared in Example XIII—C was placed in a one inch (inside diameter) vertically mounted, tubular reactor of stainless steel fitted with means for feeding gaseous acetylene and hydrogen fluoride into the reactor and removing the products from the reactor. The reactor was immersed in a molten salt bath at  $350^{\circ}\text{C}$ . A preheated mixture of hydrogen fluoride and acetylene in the molar ratio of 1.3 moles of hydrogen fluoride per mole of acetylene was fed into the reactor at the rate of 45.3 ml. acetylene/g.catalyst/hr. at atmospheric pressure. The product issuing from the reactor was scrubbed with dilute aqueous potassium hydroxide, dried and analyzed by means of a mass spectrometer. Alternatively, the hydrogen fluoride can be separated from the other products by fractional distillation at atmospheric pressure using a condenser temperature of from  $-20^{\circ}\text{C}$ . to  $0^{\circ}\text{C}$ . The results tabulated below indicate the composition of the acid free product at the end of the first and fourth hours of operation along with the conversions and yields indicated thereby.

50

55

60

65

70

## RESULTS

Time on Stream	1 hr.	4 hrs.
<i>Mole % Products (acid free)</i>		
<i>Vinyl Fluoride</i>	74.8	75.4
<i>1,1-Difluoroethane</i>	10.7	8.9
<i>Acetylene</i>	4.7	6.5
<i>Propylene</i>	1.1	0.4
<i>Ethylene</i>	8.2	7.6
<i>Ethane</i>	0.5	0.2
<i>Propane</i>	0.1	0.05
<i>% Conversion</i>	95.8	93.98
<i>% Yield</i>		
<i>Vinyl Fluoride</i>	69.8	74.3
<i>1,1-Difluoroethane</i>	10.0	8.3
<i>By-products</i>	20.2	17.0

Essentially no water or tar was formed during the period of operation.

EXAMPLE XV  
5 The acetylene feed rate of Example XIV

was increased to 67.9 ml. acetylene/g./hr. at 350°C., at a mole ratio of 1.3. After 4 hours of operation, the product had the following composition.

## RESULTS

<i>Mole % Products</i>	
<i>Vinyl Fluoride</i>	77.0
<i>1,1-Difluoroethane</i>	11.9
<i>Acetylene</i>	5.6
<i>Propylene</i>	0.1
<i>Ethylene</i>	5.1
<i>Ethane</i>	0.1
<i>% Conversion</i>	94.7
<i>% Yield</i>	
<i>Vinyl Fluoride</i>	77.2
<i>1,1-Difluoroethane</i>	12.0
<i>By-products</i>	10.8

Examples XIV and XV are illustrative of the case where feed rates have little effect on conversion as explained hereinbefore.

**EXAMPLE XVI**  
Example XIV was repeated using a feed rate of 29.7 ml. acetylene/g./hr., 350°C. and a mole ratio of 2.5. The following results were obtained after four hours of operation. 5

#### RESULTS

##### Mole % Products

<i>Vinyl Fluoride</i>	68.0
<i>1,1-Difluoroethane</i>	21.2
<i>Acetylene</i>	4.7
<i>Propylene</i>	0.3
<i>Ethylene</i>	5.6
<i>Ethane</i>	0.2
% Conversion	95.6
% Yield	
<i>Vinyl Fluoride</i>	66.7
<i>1,1-Difluoroethane</i>	20.8
<i>By-products</i>	12.5

- 10 Comparing this example with Example XIV, which differs only in the mole ratio, shows that the primary effect of a larger mole ratio is to increase the yield of 1,1-difluoroethane at the expense of vinyl fluoride.

**EXAMPLE XVII**  
Example XIV was repeated with the sole change of the reaction temperature from 350° to 400°C. Under these conditions the product had the following composition after four hours operation. 15 20

#### RESULTS

##### Mole % Product

<i>Vinyl Fluoride</i>	66.4
<i>1,1-Difluoroethane</i>	8.9
<i>Acetylene</i>	15.7
<i>Ethylene</i>	8.7
<i>Ethane</i>	0.4
% Conversion of Acetylene	85.7
% Yield	
<i>Vinyl Fluoride</i>	70.7
<i>1,1-Difluoroethane</i>	9.5
<i>By-products</i>	19.8

This example illustrates the higher by-product yield which accompanies higher temperatures.

#### EXAMPLE XVIII

- 5 Using the reaction system of Example XIV, 237 g. of activated alumina (F-10 grade of Alcoa) was placed in the reactor. The reactor was then heated to 350°C. in the molten salt

bath and a preheated mixture of hydrogen fluoride and acetylene in the mole ratio of 1.3:1 was passed into the reactor at a rate of 45.2 ml. acetylene/hr./g. of catalyst. The product was treated as in Example XIV. There was some tar formed. The composition of the gaseous product was determined after one and four hours of operation with the results shown below.

10

15

#### RESULTS

Time on Stream	1 hr.	4 hrs.
<i>Mole % Product</i>		
<i>Vinyl Fluoride</i>	19.3	56.6
<i>1,1-Difluoroethane</i>	13.1	—
<i>Acetylene</i>	34.5	17.7
<i>Propylene</i>	9.7	9.4
<i>Ethylene</i>	21.4	13.2
<i>Ethane</i>	1.4	0.8
<i>Propane</i>	0.4	0.5
<i>Butene</i>	—	1.8
<i>% Conversion</i>	76.1	87.4
<i>% Yield</i>		
<i>Vinyl Fluoride</i>	17.5	46.1
<i>1,1-Difluoroethane</i>	11.9	0
<i>By-products</i>	70.6	53.9

- 20 By comparison of the results obtained at four hours with the results obtained at one hour, it is readily apparent that the catalyst improves with time. Compare however the results of this example with those of Example XIV. The only difference between Example XIV and Example XVIII is the pretreatment of the catalyst used in Example XIV. The time of use has only a slight effect on the results of Example XIV and the yields obtained are far superior to those obtained in Example XVIII. It is quite surprising that a
- 25
- 30

simple pretreatment should produce such a remarkably superior catalyst, particularly since the disclosure in U.S. 2,471,525 does not indicate that there is any difference between aluminum oxide and aluminum fluoride as catalyst materials.

#### EXAMPLE XIX

Example XIV was repeated at 4 atm. abs. pressure with a flow rate of 115.5 ml. acetylene (at 25°C. and one atmosphere)/g. catalyst/hr. and a mole ratio of HF/acetylene of 1.63. The results are shown below.

35

40

## RESULTS

*Mole % Products*

<i>Vinyl Fluoride</i>	54.7
<i>1,1-Difluoroethane</i>	29.8
<i>Acetylene</i>	7.6
<i>Ethylene</i>	0.8
<i>Propylene</i>	0.1
<i>Ethane</i>	0.05
<i>% Conversion</i>	91.9
<i>Vinyl Fluoride</i>	63.2
<i>1,1-Difluoroethane</i>	34.4
<i>By-products</i>	1.1

## EXAMPLE XX

The catalyst of Example XIII—C (5.0 g.) was 1.3 moles HF per mole of acetylene and was placed in an 0.9×20.3 cm. tubular reactor fitted in the same manner as the previous examples. Preheated acetylene and hydrogen fluoride were passed into the reactor which was heated at 325°C. The mole ratio

10

was 1.3 moles HF per mole of acetylene and the feed rate of acetylene was 3600 ml. (at standard conditions)/gram catalyst/hr. The reaction pressure was 3 atm. abs. The product was recovered as before. The results are shown below.

## RESULTS

*Mole % Product*

<i>Vinyl Fluoride</i>	79.5
<i>1,1-Difluoroethane</i>	16.7
<i>Acetylene</i>	3.0
<i>Ethylene</i>	0.9
<i>% Conversion</i>	97.0
<i>% Yield</i>	
<i>Vinyl Fluoride</i>	81.2
<i>1,1-Difluoroethane</i>	17.0
<i>Ethylene</i>	1.8

It is understood that the preceding examples are representative and that said examples may be varied within the scope of the total specification, as understood by one skilled in the art, to produce essentially the same result.

**WHAT WE CLAIM IS:—**

1. A process for preparing vinyl fluoride and 1,1 - difluoroethane which comprises passing a mixture of hydrogen fluoride and acetylene at a temperature of from 250°C to 400°C and at a pressure of from 0.1 to 4 atmospheres absolute over beta or gamma-aluminium fluoride catalyst or a mixture thereof with delta-aluminium fluoride catalyst, the mixture of hydrogen fluoride and acetylene having a molar ratio of from 1 to 5 moles of hydrogen fluoride per mole of acetylene and the feed rate of acetylene in the mixture being from 10 to about 4,000 millilitres, measured at standard conditions, per gram of catalyst per hour, and recovering vinyl fluoride and 1,1-difluoroethane from the reaction mixture.
2. A process according to claim 1 in which the mixture of beta, gamma and delta-aluminium fluoride catalysts is obtained by treating aluminium chloride with anhydrous hydrogen fluoride at from 25°C to 380°C until replacement of chlorine by fluorine is substantially complete.
3. A process according to claim 1 in which the catalyst is obtained by passing anhydrous hydrogen fluoride at from about 200°C to about 500°C over an aluminium oxide catalyst until from 0.3 moles to 6 moles of hydrogen

fluoride per mole of aluminium oxide have reacted with the aluminium oxide.

4. A process according to claim 1 in which the catalyst is obtained by passing anhydrous hydrogen fluoride at from 200°C to 500°C over an aluminium oxide catalyst until water ceases to be formed.

5. A process according to claim 3 or 4 in which the hydrogen fluoride is passed over the aluminium oxide catalyst at a temperature of 300°C.

6. A process according to any of claims 1 to 5 in which the mixture of hydrogen fluoride and acetylene is passed over the catalyst at a temperature of from 300°C to 350°C and at a pressure of from 2 to 4 atmospheres absolute, the mixture of hydrogen fluoride and acetylene having a molar ratio of 1.3 moles of hydrogen fluoride per mole of acetylene and the feed rate of acetylene in the mixture being from 10 to 400 millilitres, measured at standard conditions, per gram of catalyst per hour.

7. A process for preparing vinyl fluoride and 1,1 - difluoroethane according to any of claims 1 to 6 substantially as herein described in any of the Examples.

8. Vinyl fluoride and 1,1 - difluoroethane when produced by the process claimed in any of the preceding claims.

A. A. THORNTON & CO.,

Chartered Patent Agents,

Northumberland House,

303—306, High Holborn, London, W.C.1,

For the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

**THIS PAGE BLANK (USPTO)**